



# Chelating Agents as Electrolyte Additives for Lithium-Ion Batteries

Donald L. Foster, Jeff Wolfenstine, Wishvender K. Behl

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Sensors and Electron Devices Directorate

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## Abstract

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Pentamethyldiethylenetriamine (PMDT), tetraglyme, and the crown ether 12-Crown-4 (12-Cr-4) were investigated as electrolyte additives for lithium-ion cells using graphite anodes. Cyclic voltametry at glassy carbon electrodes in 1 mol/L  $\text{LiPF}_6$ /propylene carbonate (PC) solutions containing PMDT, 12-Cr-4, or tetraglyme additives showed that the PMDT additive was electrochemically oxidized at  $\sim 3.5$  V versus lithium reference. The electrolytes with 12-Cr-4 and tetraglyme, on the other hand, were found to be stable up to  $\sim 4.5$  V, where the control electrolyte without any additive was oxidized. Ionic conductivity measurements of the same solutions showed that all three additives enhanced the conductivity of 1 mol/L  $\text{LiPF}_6$ /PC solution at 25 °C. Lithium cycling studies in PC solutions using graphite electrodes showed that the 12-Cr-4 and tetraglyme additives allowed reversible lithium intercalation into graphite; whereas, the PMDT additive did not have any effect. However, the PMDT additive was found to reduce the irreversible capacity loss on the first cycle in ethylene carbonate-propylene carbonate electrolyte solutions.

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# 1. Introduction

It has been reported [1–11] that adding ligands, such as the crown ether 12-Crown-4 (12-Cr-4) or tetraglyme, to electrolytes of lithium-ion cells and batteries with graphite negative electrodes can prevent the cointercalation of solvent molecules with lithium in graphite layers. These additives can also allow reversible intercalation of lithium into graphite in electrolytes containing solvents that do not form stable passivating solid electrolyte interface (SEI) films on carbon, such as propylene carbonate (PC). The large crown ether or tetraglyme molecules tightly chelate the lithium ions and prevent the solvent molecules from passing into the graphite layers along with lithium ions. Unfortunately, crown ethers are too costly and toxic to be used as additives in practical battery electrolytes for commercial or military applications.

Another class of large chelating ligands that could be used as electrolyte additives is complex tertiary amines, such as N,N,N',N',N''-pentamethyldiethylenetriamine (PMDT), N,N,N',N'',N''',N''''-hexamethyltriethylenetetraamine (HMTT), or N,N,N',N' - tetramethylethylenediamine (TMED). It was shown [12,13] that these compounds could complex lithium ion so that lithium salts with lattice energies as high as 210 kcal per mole could be dissolved in very nonpolar solvents such as toluene. Laboratory cells with electrolytes consisting of amine chelated lithium salts dissolved in aromatic hydrocarbons were made and discharged, although conductivities were too low for practical application. Whitney and Foster [14] later showed that adding as little as 10 percent of a polar solvent, such as propylene carbonate, could increase the conductivity of electrolyte solutions, such as 1 mol/L PMDT:LiAsF<sub>6</sub>/PC-toluene, by over an order of magnitude, making these solutions suitable as battery electrolytes. These complex amines are far less expensive than crown ethers and may have similar beneficial effects on reversible intercalation of lithium into graphite. Tertiary amines as electrolyte additives are much less well known in the electrochemical community and their use in lithium-ion batteries has not been explored.

## 2. Experimental Procedures

We used lithium hexafluorophosphate ( $\text{LiPF}_6$ , Hashimoto, Japan)\* and SFG-44 graphite (Timcal Ltd) as received from suppliers. Ethylene carbonate (EC) and PC (Grant Chemical Co), tertiary polyamine PMDT, 12-Cr-4, and tetraglyme (all from Aldrich Chemical Co) were dried over 4A molecular sieves and verified by Karl-Fischer coulometric titration to have moisture concentration of less than 20 p/m before use. We conducted all work in a Vacuum Atmospheres Nexus One glove box with the argon atmosphere continuously monitored to be less than 0.5 p/m moisture/oxygen.

We determined the ionic conductivity of the following solutions: (1) 1 mol/L  $\text{LiPF}_6$ /PC, (2) 1 mol/L  $\text{LiPF}_6$ :1 mol/L PMDT/PC, (3) 1 mol/L  $\text{LiPF}_6$ :1 mol/L 12-Cr-4/PC, and (4) 1 mol/L  $\text{LiPF}_6$ :1 mol/L tetraglyme/PC. The conductance was measured with two-electrode sealed glass conductivity cells with platinum electrodes at temperatures of  $-30$ ,  $0$ , and  $25$  °C at a frequency of 1 kHz. We allowed the system to equilibrate for 3 hr at each temperature before conductance measurements were recorded. We determined the cell constant using a standard aqueous potassium chloride solution at  $25$  °C and determined the conductivity using the calculated cell constant.

We examined the electrochemical stability of  $\text{LiPF}_6$  in PC solutions containing PMDT, 12-Cr-4, and tetraglyme additives by recording linear sweep voltammograms in these solutions at smooth glassy carbon electrodes (electrode area:  $0.0792 \text{ cm}^2$ ). Then we performed voltametric scans using an EG&G Instruments, Inc, Princeton Applied Research (PAR) potentiostat/galvanostat (model 273). The experiments were computer-controlled with EG&G PAR electrochemical analysis software (model 270).

We doctor bladed graphite SFG 44 (Timcal Ltd) electrodes on electrodeposited copper foil (All Foils, Inc) substrates using a 5 percent polyvinylidene fluoride (PVDF) binder. The graphite electrodes were vacuum dried at  $120$  °C for over 24 hr before use.

We performed lithium intercalation and deintercalation in graphite by cycling graphite flag electrodes versus lithium electrodes in sealed glass cells in the glove box. The cells were cycled with an Amel model 546 galvanostat/electrometer at a current density of  $28 \mu\text{A}/\text{cm}^2$  for all lithium cycling experiments. We verified the currents using a Hewlett-Packard model 3435A digital multimeter.

To learn more about the passivating films formed on the graphite electrodes in electrolytes containing the additives, we moved the graphite electrodes after the first cycle from an electrolyte containing an additive to the same electrolyte without the additive. To ensure that no residual additive remained on the electrode being transferred, we soaked the electrodes in solvent only, either PC or EC:PC, for 24 hr, without salt or additive. The second cycle was done in an electrolyte without the additive.

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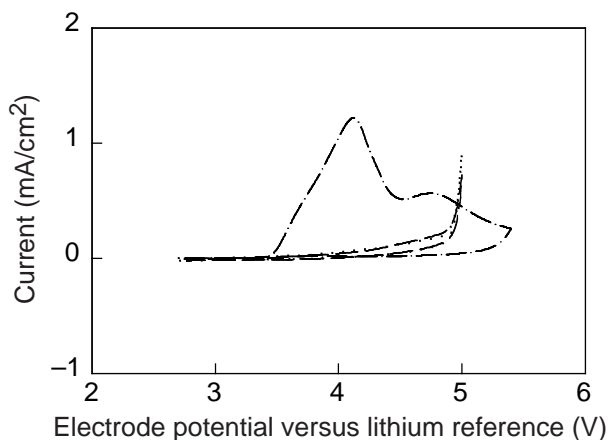
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### 3. Results and Discussion

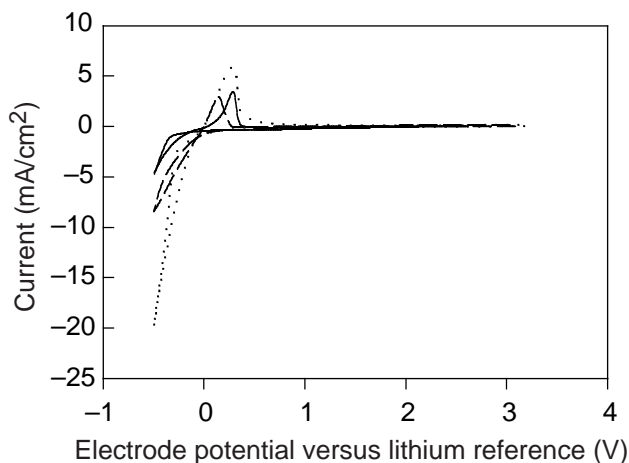
Figures 1 and 2 show typical voltammograms obtained at a scan rate of 20 mV/s on glassy carbon electrodes in electrolytes with different additives. The results show that solutions containing PMDT were stable only up to a potential of about 3.5 V, where the amine starts to oxidize. The solutions containing 12-Cr-4 or tetraglyme additives were stable to 4.5 V, where the control electrolyte with no additive also oxidizes. Figure 2 shows that lithium metal deposition and dissolution occurred for solutions containing any of the three additives during the cathodic scan.

Figure 3 shows the effect of the PMDT, crown-ether, and tetraglyme additives on the conductivity of 1 mol/L LiPF<sub>6</sub>/PC electrolyte versus temperature. Figure 3 reveals several important points. First, all the additives increased the conductivity of the LiPF<sub>6</sub>/PC solution at all temperatures except -30 °C, where the LiPF<sub>6</sub>/PC solutions with and without the 12-Cr-4 additive have the same value. Second, solutions containing the 12-Cr-4 and tetraglyme additives have similar conductivities at all temperatures over the entire temperature range. Third, PMDT gives the largest increase in conductivity of the three additives.

**Figure 1.** Anodic voltammograms obtained at glassy carbon electrodes in 1 mol/L LiPF<sub>6</sub>/PC containing PMDT (dot dash), 12-Cr-4 (dash), and tetraglyme (dot) at a scan rate of 20 mV/s.



**Figure 2.** Cathodic voltammograms obtained at glassy carbon electrodes in 1 mol/L LiPF<sub>6</sub>/PC containing PMDT (solid), 12-Cr-4 (dash), and tetraglyme (dot) at a scan rate of 20 mV/s.





**Figure 3. Conductivity of 1 mol/L  $\text{LiPF}_6$  electrolytes with and without additives.**

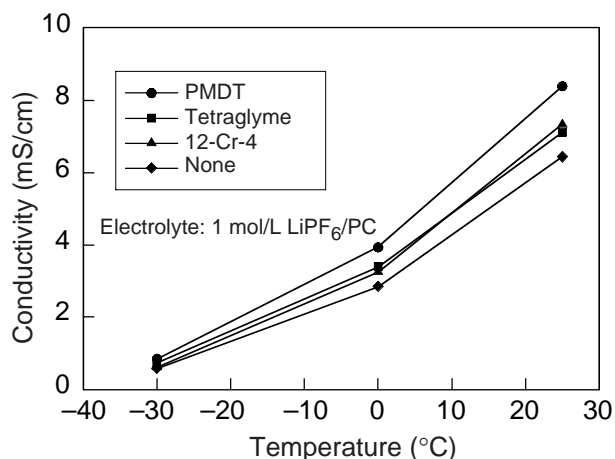
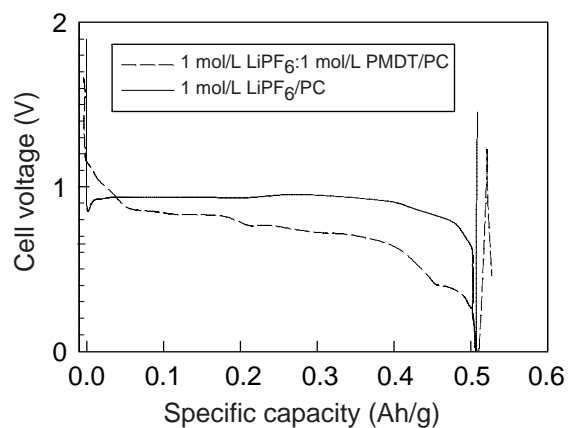


Figure 4 shows the charge-discharge curve for a graphite electrode versus lithium in 1 mol/L  $\text{LiPF}_6$ /PC and 1 mol/L  $\text{LiPF}_6$ :1 mol/L PMDT/PC electrolytes. It shows an extensive exfoliation of the graphite electrode and it also shows that reversible capacity is not obtained in either electrolyte. The overall behavior is essentially the same with or without the additive.

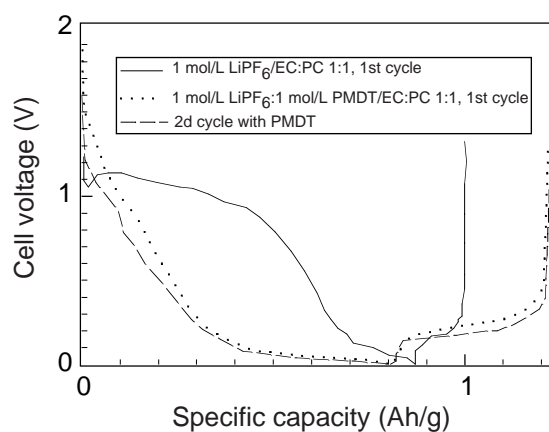
Figure 5 shows the charge-discharge curve for a fresh graphite electrode in 1 mol/L  $\text{LiPF}_6$ /EC:PC (1:1 by volume) and 1 mol/L  $\text{LiPF}_6$ :1 mol/L PMDT/EC:PC (1:1 by volume). The presence of the PMDT additive increases the reversible capacity and reduces exfoliation compared to the electrolyte without the additive. Interestingly, the plateaus that are characteristic of staging reactions in graphite are not present in the curve for the graphite electrode in the amine containing electrolyte. After the first cycle in the electrolyte containing PMDT, we washed the graphite electrode in EC:PC as previously described and then cycled in 1 mol/L  $\text{LiPF}_6$ /EC:PC with no additives. The electrode intercalated lithium readily with no exfoliation. Again, the staging plateaus are absent from the curves. The performance was similar to the first cycle with the additive. Clearly, there is more reversible capacity than can be achieved in electrolyte without the PMDT additive, indicating that a stable SEI was formed during the first cycle that prevents further intercalation of solvent molecules into graphite.

Figure 6 shows the results for the cycling data in 1 mol/L  $\text{LiPF}_6$ :1 mol/L 12-Cr-4/PC. The charge-discharge curves show very distinct staging plateaus for intercalation and deintercalation of lithium into graphite. After one cycle, we removed the graphite electrode from the electrolyte and washed it in PC; then we cycled in the electrolyte without the additive. These cycling data results are also shown in figure 6, and it is seen that there was no reversible capacity. Extensive exfoliation destroyed the graphite electrode.

**Figure 4. Voltage profiles of first cycle for Li/graphite cell in 1 mol/L  $\text{LiPF}_6$ /PC electrolyte with and without PMDT additive.**



**Figure 5. Voltage profiles of Li/graphite cells in 1 mol/L  $\text{LiPF}_6$ /EC:PC 1:1 with and without PMDT additive.**



**Figure 6. Voltage profiles of first cycle Li/graphite cell with 1 mol/L  $\text{LiPF}_6$ :1 mol/L 12-Cr-4/PC and second cycle in electrolyte without 12-Cr-4 additive.**

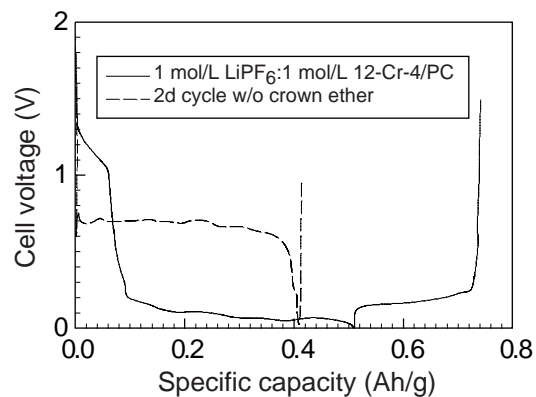


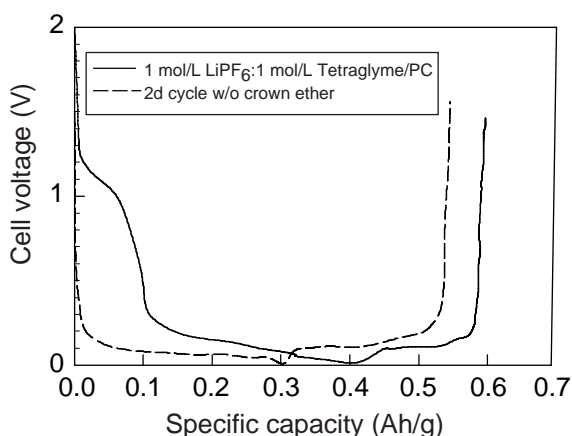
Figure 7 shows that lithium intercalated reversibly into graphite in 1 mol/L  $\text{LiPF}_6$ :1 mol/L tetraglyme/PC electrolytes. Subsequently switching the electrolyte solution to 1 mol/L  $\text{LiPF}_6$ /PC does not change the result, indicating that a stable SEI was formed in the first cycle. The results for cells with tetraglyme additive are similar to the results for the amine additives in that no plateaus are associated with staging in the charge-discharge curves.

We observed that all three additives increase the ionic conductivity of the  $\text{LiPF}_6$ /PC electrolyte. 12-Cr-4 [10] and PMDT [14] have been used in the past as ionic conductivity enhancers, and both have strong affinity for  $\text{Li}^+$  ions in solution [7,10,12–14]. These complexes reduce the amount of ion association (i.e., formation of neutral complexes) and hence lead to an increase in ionic conductivity. The higher conductivity of the PMDT solution may be because PMDT complexes the  $\text{Li}^+$  ions more strongly than 12-Cr-4, allowing greater dissociation of neutral complexes.

The results of the cycling studies on Li/graphite cells show that although all three ligands (PMDT, 12-Cr-4, and tetraglyme) result in some improvement in the lithium cycling, fundamental differences exist in the behavior of lithium intercalation into graphite in electrolytes with different additives.

Several groups have studied the effect of the electrolyte additive 12-Cr-4 on the graphite intercalation of lithium ion in PC or EC:PC solvent electrolytes [7,10–11]. According to the model proposed by Aurbach et al [7], improvement in reversible capacity is due to the strong affinity of 12-Cr-4 to the lithium ion. This prevents the lithium ion from dragging PC molecules into the graphite layers and causing exfoliation before a passivating SEI layer is formed on the graphite surface. In situ Fourier transform infrared (FTIR) studies [7] confirmed that only the solvent molecules were reduced on the electrode surface to form the SEI and not 12-Cr-4. Reversible intercalation of lithium can even be achieved when the concentration of 12-Cr-4 is as little as one-tenth of the lithium-ion concentration, because lithium ions complexed by 12-Cr-4 are more mobile.

**Figure 7. Voltage profile of first cycle for Li/graphite cell in a 1 mol/L  $\text{LiPF}_6$ :1 mol/L tetraglyme/PC electrolyte and second cycle without tetraglyme additive.**



Because we found no reversible capacity in the PC-based electrolyte containing the PMDT additive suggests that although the amine ligand has strong affinity for the lithium ion (as evidenced by the conductivity data), it does not completely dissociate the lithium ion from the propylene carbonate; thus it allows some PC to cointercalate into the graphite layers. If ethylene carbonate is present in the electrolyte, then these results suggest that PMDT sufficiently hinders cointercalation of solvent molecules into the graphite layers until a stable SEI layer is formed on the carbon from the reduction of ethylene carbonate. Therefore, switching to the electrolyte without the additive for the second cycle does not affect the result, because a stable SEI has already been formed during the first cycle.

The results on the first cycle for the cells containing 12-Cr-4 electrolyte are similar to results obtained by other researchers [7,10–11]. The crown ether ligand allows the reversible lithium intercalation with some irreversible capacity loss on the first cycle. The results for the second cycle after the electrode was switched to an electrolyte containing no crown ether are not consistent with the formation of a stable SEI layer. This is in contrast to the suggestions by other researchers [4,7,10] who maintain that a stable SEI layer is formed. The material reduced on the carbon surface during the first cycle does not prevent the cointercalation of PC into the graphite layers once crown ether is no longer present in the electrolyte. The results suggest that cointercalation of solvent is prevented when 12-Cr-4 is present by the very complete solvation of lithium by the crown ether excluding other solvent molecules, particularly PC, from cointercalating in graphite. The film, however, only passivates outer graphite surface and does not prevent cointercalation of PC if 12-Cr-4 is not present in the electrolyte.

The results for graphite cycling in 1 mol/L LiPF<sub>6</sub>:1 mol/L tetraglyme/PC shown in figure 7 are similar to the results for electrolyte with the 12-Cr-4 additive. Reversible capacity is readily achieved in electrolytes with a PC solvent. After switching to an electrolyte without tetraglyme additive, we achieved reversible capacity on the second cycle indicating that unlike the crown ether, a stable SEI interface is formed on the graphite surface.

The charge-discharge curves for the graphite electrode in electrolyte containing the 12-Cr-4 additive show the familiar plateaus associated with lithium staging within graphite. The plateaus are noticeably absent if PMDT or tetraglyme is present as an additive in the electrolyte. Their absence could be due to cointercalation of these large ligands into the graphite layers inhibiting the formation of stages. Concentration of tetraglyme at the graphite interface would be somewhat lower than 12-Cr-4 if the tetraglyme is cointercalated and the 12-Cr-4 does not go into the graphite layers. This could be why a more passivating film is formed in electrolytes containing tetraglyme than in electrolytes containing 12-Cr-4 additive.

## 4. Conclusions

The results of the voltametric scans show that PMDT cannot be used as an additive to  $\text{LiPF}_6/\text{PC}$  electrolytes above 3.5 V versus lithium because it will oxidize at the positive electrode at that potential. Similar studies with 12-Cr-4 and tetraglyme additives have shown that these materials are as stable in solution as the PC or EC solvents, which oxidize at  $\sim 4.5$  V.

We investigated the electrochemical behavior of Li/graphite cells using 1 mol/L  $\text{LiPF}_6/\text{PC}$  electrolyte with and without 1 mol/L PMDT, 1 mol/L 12-Cr-4, and 1 mol/L tetraglyme additives. Electrolytes containing the PMDT additive do not allow reversible intercalation of lithium if PC is the only solvent. In mixed EC:PC solvents, however, extensive intercalation of lithium into carbon can be achieved with the PMDT additive, and the irreversible capacity loss is considerably less with the PMDT additive present. PMDT was also shown to be the most effective conductivity enhancer of the three additives in 1 mol/L  $\text{LiPF}_6/\text{PC}$  electrolytes.

The 12-Cr-4 is an effective additive for improving the intercalation of lithium into graphite, as described in the literature [7,10–11]. However, our results indicate that the film formed on the graphite surface is not sufficient to prevent PC molecules from being cointercalated into the graphite layers. Thus, the successful intercalation of lithium into carbon in PC electrolytes containing the 12-Cr-4 additive must be explained by a mechanism other than the formation of a passivating film on the electrode surface.

Cells with electrolyte containing a tetraglyme additive showed the best overall performance on lithium cycling. Unlike 12-Cr-4, this additive allows a stable film to form on the first cycle, which prevents further solvent intercalation. Tetraglyme also has a quite significant cost advantage over 12-Cr-4, is stable to much higher potentials than PMDT, and improves the conductivity of the electrolyte. In the search for new electrolytes for lithium-ion batteries, tetraglyme may play an important role as an electrolyte component.

## Acknowledgment

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13. ABSTRACT (Maximum 200 words) Pentamethyldiethylenetriamine (PMDT), tetraglyme, and the crown ether 12-Crown-4 (12-Cr-4) were investigated as electrolyte additives for lithium-ion cells using graphite anodes. Cyclic voltammetry at glassy carbon electrodes in 1 mol/L LiPF <sub>6</sub> /propylene carbonate (PC) solutions containing PMDT, 12-Cr-4, or tetraglyme additives showed that the PMDT additive was electrochemically oxidized at ~3.5 V versus lithium reference. The electrolytes with 12-Cr-4 and tetraglyme, on the other hand, were found to be stable up to ~4.5 V, where the control electrolyte without any additive was oxidized. Ionic conductivity measurements of the same solutions showed that all three additives enhanced the conductivity of 1 mol/L LiPF <sub>6</sub> /PC solution at 25 °C. Lithium cycling studies in PC solutions using graphite electrodes showed that the 12-Cr-4 and tetraglyme additives allowed reversible lithium intercalation into graphite; whereas, the PMDT additive did not have any effect. However, the PMDT additive was found to reduce the irreversible capacity loss on the first cycle in ethylene carbonate-propylene carbonate electrolyte solutions.				
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